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HYDROGEN-OXYGEN ELECTRODE STUDY

Contract AF 33(657)-7564
Quarterly Technical Progress Report No. 6
15 June 1963

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Project Director

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SUMMARY

Porous nickel (Clevite Corporation #3 Porous Nickel) electrolyte fuel cells were operated with an asbestos electrolyte holder impregnated with both free 30% KOH and gelled 15% and 20% KOH. Indications were that gelled KOH had less mobility than the free electrolyte and would not wet or drown electrodes as quickly as free electrolyte unless mechanical pressure was applied to force the gel into an electrode. Better contact was obtained between the electrode and the electrolyte holder when KOH gel was used. Higher current densities and less polarization were experienced at 60-70 C than at room temperature. A gel of 20% KOH produced better results than one of 15% KOH. High open circuit potentials were obtained with gelled electrolyte. The major problems were dehydration of the KOH saturated electrolyte holder and the inability of the cell to support heavy loads.

Single electrode studies were carried out which showed that by reversing the electrical polarity of the fuel cell for brief intervals and driving it in the opposite direction, thus forming hydrogen at the anode and oxygen at the cathode by electrolysis, the polarization of the anode at given current densities could be reduced. Ways and means of stabilizing the electrode electrolyte contact are discussed.

INTRODUCTION

It was reported earlier that free KOH electrolyte will drown catalyzed Clevite #3 porous nickel very quickly. This ability or property of this material to absorb aqueous KOH also permits elimination of water from the electrolyte or reaction sites by diffusion to the back surface of the electrode and removal in the exit stream of fuel gas. Since the electrolyte is so mobile in Clevite #3 nickel and since a three phase contact is necessary at each electrode in the low temperature liquid electrolyte fuel cell, it is important to stabilize the electrode electrolyte contact zone in order to obtain optimum power from the cell. This can be done by applying antiwetting agents, by maintaining a water balance in the electrode, possibly by immobilizing the electrolyte with a gelling agent, by altering the structure of the electrode to get an even distribution of micropores at the electrolyte surface and possibly in other ways. This report deals with an attempt to stabilize the electrode electrolyte contact by gelling the electrolyte and using an asbestos electrolyte support. These electrolyte forms were tested in operating hydrogen oxygen fuel cells. Electrode preparation was kept constant.

EXPERIMENTAL

The procedure for electrode activation consisted of soaking the electrodes in three per cent solution of chloroplatinic acid with ultrasonic vibration of the vessel and contents for thirty minutes followed by one and a half hours standing at 43°C, drying at 100-120°C, heating in vacuum to about 450°C, cooling in vacuum, reduction in hydrogen until effluent gas from the furnace was neutral to universal pH indicator, cooling in hydrogen, sealing the edge of the electrodes with epoxy resin and a final heating in hydrogen to 225°C just prior to placing in a fuel cell. The amount of platinum in the electrodes after this treatment was approximately .5% by weight of the electrode.

In order to immobilze the KOH electrolyte an asbestos holder was used first. A 1/32" thick pure asbestos electrolyte holder was saturated with 30% KOH so that the asbestos was just moist to the touch. It was then clamped firmly between catalyzed porous nickel electrodes and hydrogen and oxygen gases were introduced to the cell at a rate of about 200 cc/min under about 1" of water pressure and at room temperature. A plot of current density vs voltage is shown in Figure 1. The inability of the cell to support a load was attributed to an insufficient number of active sites at the electrode electrolyte contact which was due in this experiment to a great extent to the drying out of the electrolyte holder by the fuel gases flowing over the back surface of the electrodes. That such a drying mechanism does proceed efficiently with the electrode material under study has been established by other investigators (Allis-Chalmers). In addition depending on the pressure applied on the electrode electrolyte holder assembly it is possible in the beginning to drown the smaller pores which

later may lose electrolyte contact with remainder of the system as the larger pores or main chammels are dried out by the flow of fuel gases over the back of the electrode. The above two feasible mechanisms both of which can contribute to electrode polarization accentuate the importance of achieving a relatively stable electrode electrolyte contact particularly since the porous nickel electrode material has a relatively low surface area.

In a further attempt to stabilize the electrode electrolyte contact the electrolyte was gelled. The electrolyte used was KOH in the form of gelled 15 and 20% solutions. The gelling agents used in the preparation of gelled KOH were Methocel 90 HG (Dow Chemical Company), Natrasol (Hercules Powder Co.) and Indulin AT (West Virginia Pulp and Paper Company). The clearest gel was obtained with Natrasol but concentrated KOH caused decomposition of this gel on standing. The most satisfactory results from the point of view of stability, antiwetting tendencies and texture were obtained with Methocel 90 HG. This latter gel was kept (covered) with no visible signs of deterioration for at least three months. Up to the present time the highest concentration of KOH which was successfully gelled was twenty percent. The procedure which has been found suitable consisted of adding slowly and with gentle stirring 17 grams of Methocel 90 HG to 200 grams of twenty per cent KOH at approximately 90°C - additional agitation was provided by carrying out this operation having the reaction beaker in an ultrasonic bath. On cooling in a refrigerator for four hours a very viscous gel formed.

To investigate the possible application of such as electrolyte, the gel was pressed into the asbestos holder and a thin coating, .05", was left on the surface of the holder to be pressed into the electrode surface. Plots of current density vs voltage for cells containing 15% and 20% gelled

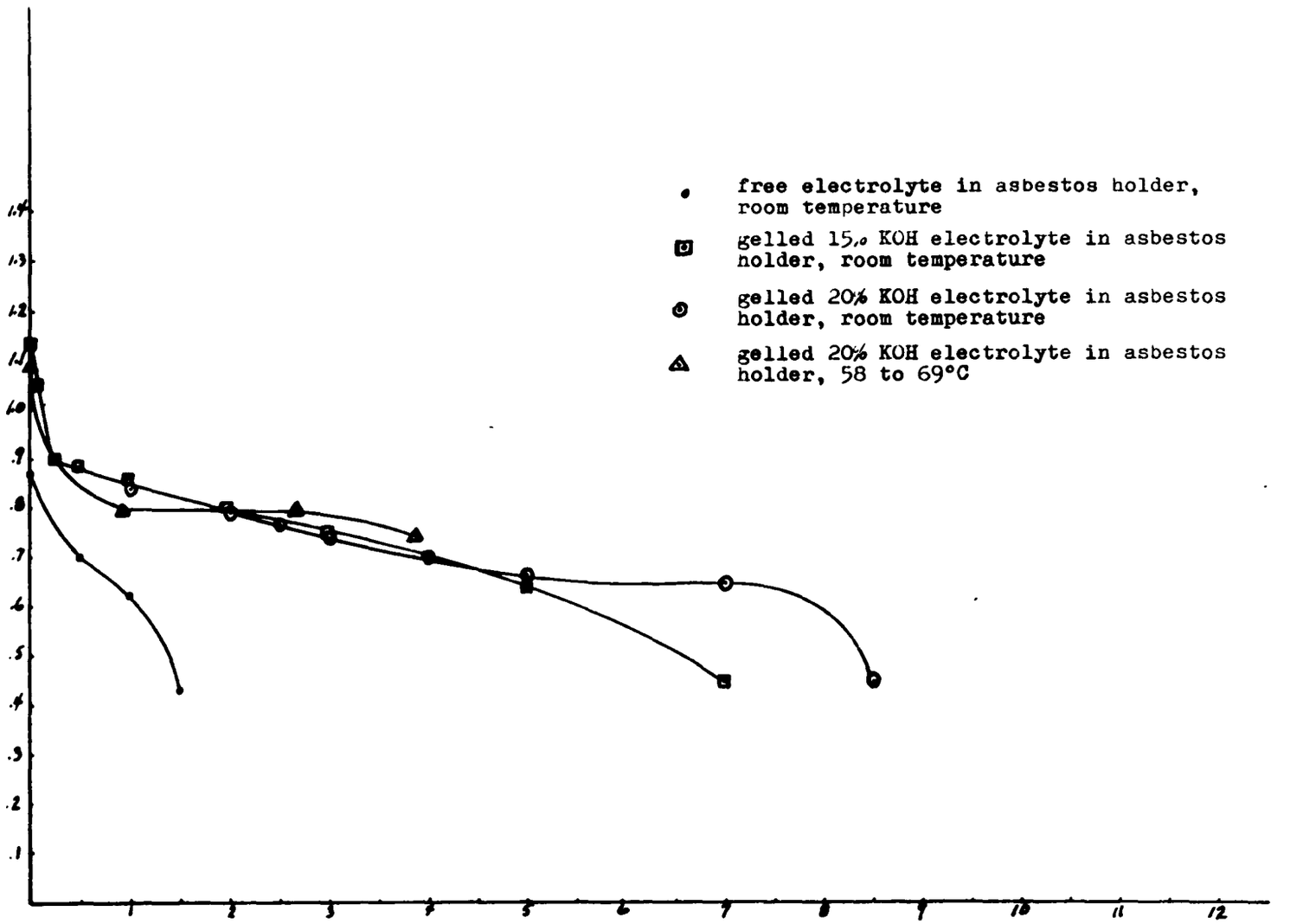

free electrolyte in asbestos holder, room temperature
gelled 15% KOH electrolyte in asbestos holder, room temperature
gelled 20% KOH electrolyte in asbestos holder, room temperature
gelled 20% KOH electrolyte in asbestos holder, 58 to 69°C

Figure 1

KOH are shown in Figure 1. The plots coincide except at higher current densities where the 20% electrolyte performs better than the 15% electrolyte.

It was found that on using gelled KOH open circuit potentials were high, 1.1 to 1.2 volts and in a few instances as high as 1.4 volts. This latter value was unexpected. Other investigations at the University of Florida Experimental Station reported high open circuit potentials on using paste electrolytes. It was observed that when a very small load was placed on those cells which gave open circuit potentials of 1.4v, the cell voltage dropped instantaneously to the order of .9v. This could infer activation polarization, or one rate controlling reaction at near equilibrium conditions and another rate controlling reaction under load conditions. If the organic gelling agent is playing a role as a reducing agent in the peroxide mechanism at the oxygen electrode it may be of interest to study this further.

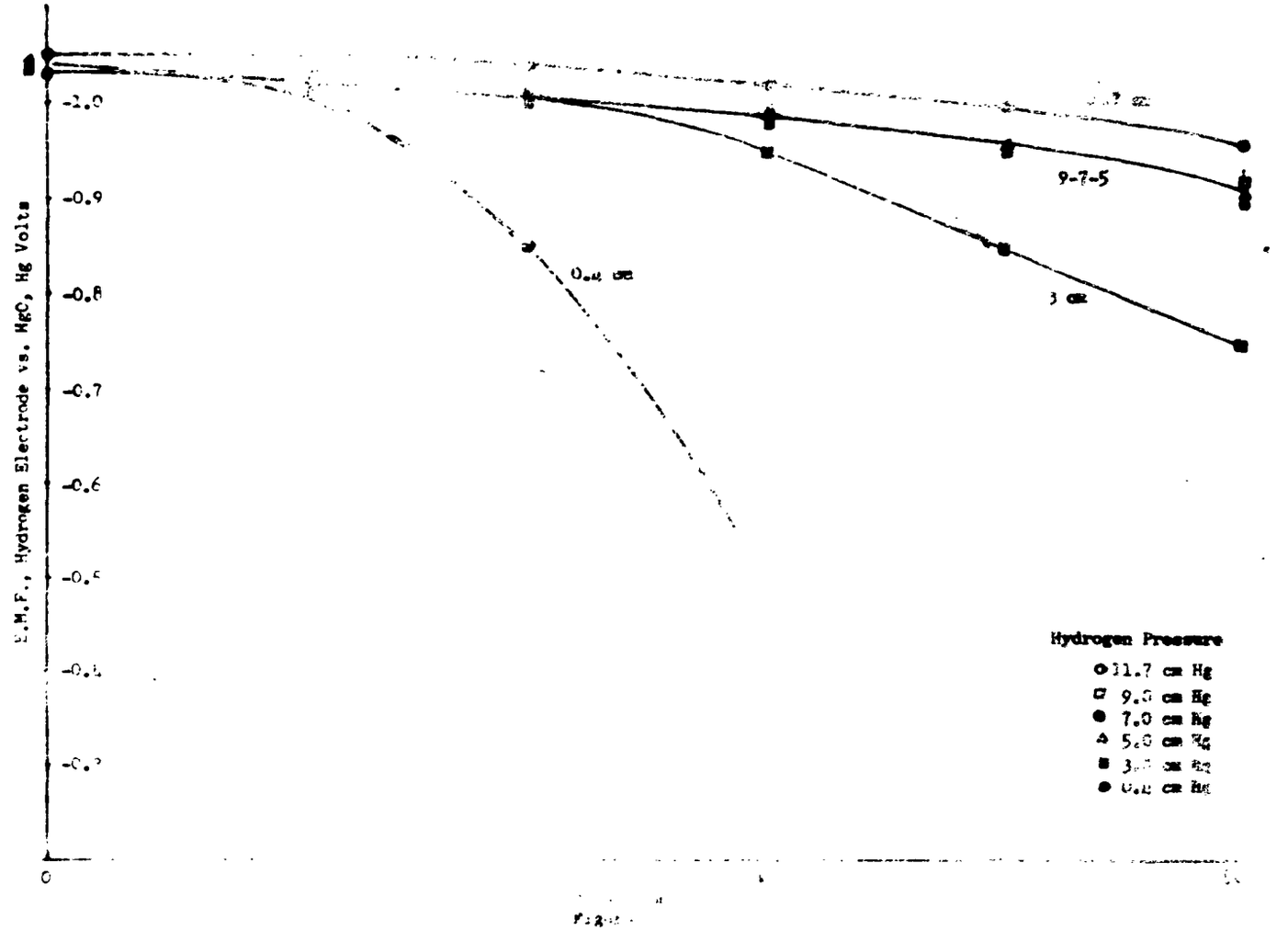
In order to take advantage of more favourable Kinetics at higher temperatures a catalytically activated porous nickel anode and cathode were used in conjunction with 20% gelled KOH electrolyte in an asbestos holder. In this experiment the fuel cell was operated at 58-69°C. The current density vs. voltage curve is plotted in Figure 1.

The improved performance of the cell under load was still not up to expectations. However, the drying out of the electrolyte holder was much faster at the higher temperatures, so much so that slugs of water formed in the gas outlets of the cell. This no doubt meant that the number of sites available for reaction was decreasing with time and limiting the current density which could be drawn.

Attempts to reduce the rate of drying by decreasing the gas flow rates resulted in a drop in cell voltage.

A separate single electode study was carried out using a catalyzed Cleviate #3 porous nickel anode in which the electolyte was held back by opposing hydrogen fuel gas pressure. The pressure differentials involved would not be expected to singificantly alter the activity of the hydrogen and therefore the results should indicate the effect of drowning on polarization of the hydrogen electrode. In the study platinum gauze was the working electrode and a dc power supply was used to drive the cell. The results are shown in Figure 2. They substantiate the claim that aqueous KOH will quite readily enter this porous nickel and drown or polarize the hydrogen electrode. In the experiments referred with gelled electrolytes this drowning problem was at its worst just after the fuel cells were assembled. It was noted in several experiments at room temperature that the cells attained their optimum operating efficiencies only after fuel gases were run through the cell for varying times up to two hours, the time being related to how much excess gelled KOH was forced into the electrodes and the gas flow rates.

It was felt that some of this solution which drowned the electrodes in the beginning could be removed by running the cell under electrolysis conditions and at the same time increase electrode activity. That is may be possible to increase the number of active sites on the electrodes prior to cell operation but subsequent to electrode preparation is indicated by Figure 3 which gives the results of a single electrode study in which the polarization of the hydrogen electrode under load was decreased by driving the electrode under electrolysis conditions for thirty seconds. The electrode polarization under load was decreased further by an additional thirty seconds under electrolysis conditions. A first attempt to do this in an actual fuel cell did not produce a significant increase in current density at room temperature.


E.M.F., Hydrogen Electrode vs. HgCl, Hg Volts
-2.0
-0.9
-0.8
-0.7
-0.6
9-7-5
3 cm
Hydrogen Pressure
11.7 cm Hg
9.0 cm Hg
7.0 cm Hg
5.0 cm Hg
0
1

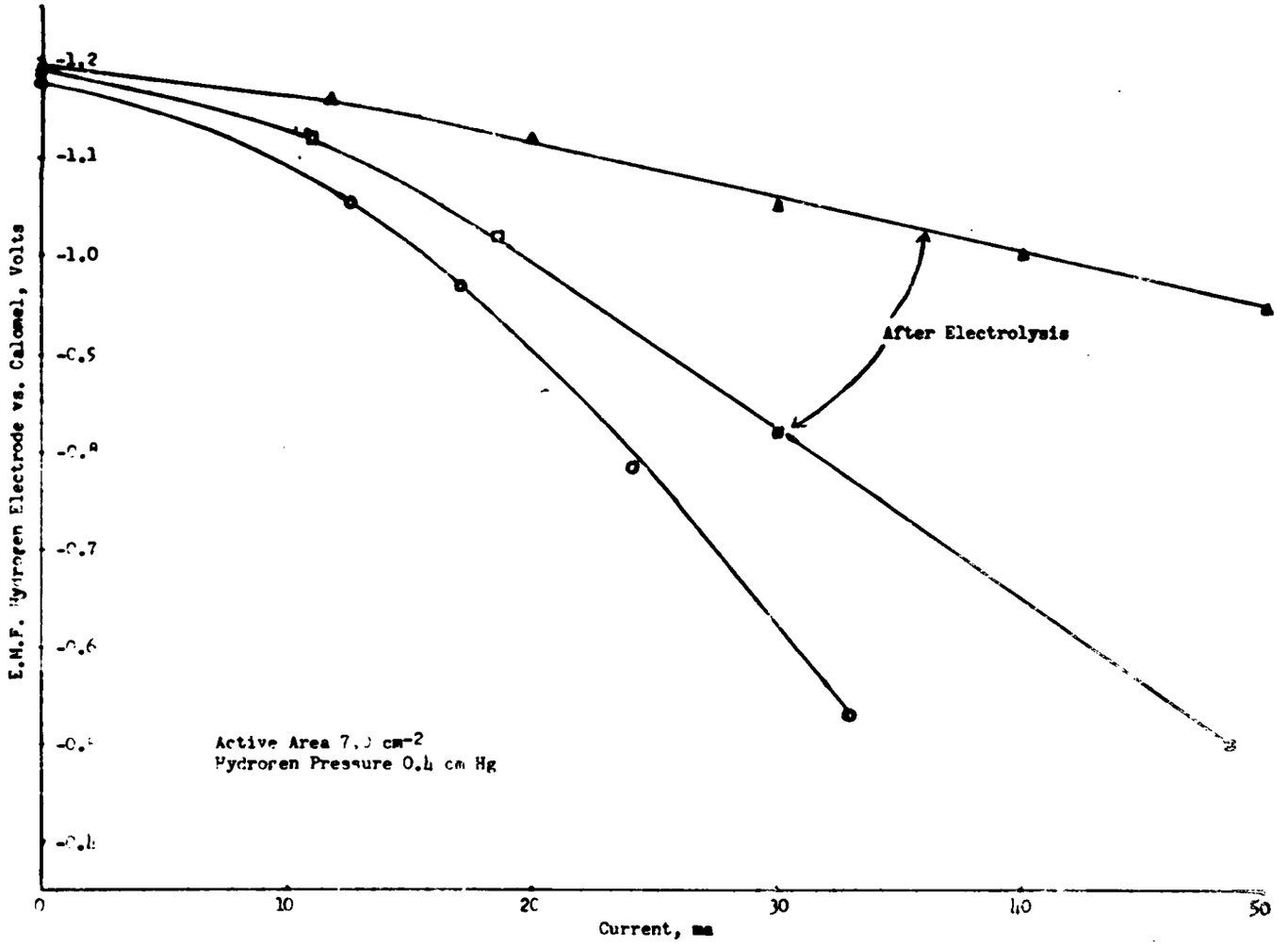

E.M.F. Hydrogen Electrode vs. Calomel, Volts
-1.2
-1.1
-1.0
-0.5
-0.8
-0.7
-0.6
-0.5
-0.4
0
10
20
30
40
50
Current, ma
After Electrolysis
Active Area 7.3 cm-2
Hydrogen Pressure 0.4 cm Hg

Figure 3

DISCUSSION

From the results obtained with gelled 20% KOH at room temperature 7 ma/cm^2 at .65v one would expect that at 100°C the current density could be increased to 50 ma/cm^2. However, the stability of electrode electrolyte contact is greatly decreased at higher temperatures such that raising the temperature slowly above 60°C caused rapid dehydration of the electrolyte. Once higher temperatures would be reached it is likely that the water formed by electrode reaction would be sufficient to cause the opposite effect, that of drowning reactions sites. The overall problem can be approached by increasing the activity of the electrodes - more active sites - or finding a technique for bringing the cell up to a high operating temperature quickly without significant loss of electrolyte (solvent water) from the asbestos holder. If the latter can be done a gelled electrolyte which is stable at 90-100°C in the presence of water vapor or high humidity, should provide a relatively stable electrode electrolyte contact. At low temperatures the gel contact with an electrode was superior to the free electrolyte in an asbestos holder contact (Figure 1). Similarly a stable high temperature gel in an asbestos holder should provide a better contact with electrodes at high temperatures and improved cell operation.

The use of antiwetting agents stable at 100°C used in conjunction with free electrolyte or gelled electrolyte in an asbestos holder also may improve the stability of the electrode electrolyte contact.

The use of electrolysis to create additional active sites should be investigated further.

In any event it is necessary to achieve some sort of balance between the water in the electrolyte and water removed from the cell by diffusion to the gas chambers and removal by exit gases. The structure of Clevite #3 porous nickel permits fairly efficient water removal by the above mechanism.